PATENT SPECIFICATION 989,025

NO DRAWINGS.

989,025

Date of Application and filing Complete Specification:
July 2, 1962. *No. 25259/62.*

Application made in Netherlands (No. 266,733) on July 5, 1961.

Complete Specification Published: April 14, 1965.

Index at Acceptance:—B6 JA6A.

Int. Cl.:—B 44 b.

COMPLETE SPECIFICATION.

Improvements in or relating to Methods of Treating Bodies of Semiconductor Material.

We, PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED, formerly Philips Electrical Industries Limited, of Abacus House, 33 Gutter Lane, London, E.C.2, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to methods of treating bodies of semiconductor material by chemically etching with an acid etching liquid which contains hydrofluoric acid and at least one oxidizing agent. Such bodies are used, for example, in the manufacture of semiconductor devices, such as transistors, crystals diodes and photoelectric cells.

In the manufacture of such devices a body of semiconductor material may be subjected to an etching treatment, for example to reduce the dimensions of the body to a required thickness, to remove certain portions, to clean the surface of the body or to polish a rough surface. Such an etching treatment may be applied to the body both prior to and subsequent to providing electrodes on the body. The etching liquid may contain as an oxidizing agent, for example, nitric acid and/or hydrogen peroxide, if desired combined with a little bromine or iodine.

When using etching liquids having high concentrations of oxidizing agents together with hydrofluoric acid etching occurs rapidly and is consequently less reproducible. Therefore, dilute aqueous solutions may be used to cause the etching treatment to occur less rapidly and in a more reproducible manner. However, it has appeared that the surface of the treated body often exhibits irregularities, for example etching pits, and may be comparatively rough. Such irregularities in the surface may have an adverse effect in the further treatment of the body in the manufacture of semiconductor devices, for example when diffusing active impurities in the body, and may in addition have a detrimental effect on the properties of such device. It has already been proposed to dilute etching liquids, which are obtained by mixing concentrated nitric acid and concentrated hydrofluoric acid, with glacial acetic acid instead of with water. This may lead to the possibility of etching pits occurring being somewhat diminished but in the case of strong dilutions with glacial acetic acid, the etching rate of this etching liquid decreases discontinuously to extremely low values when increasing the dilution.

The present invention is based on the recognition of the fact that the formation of irregularities in the surface in the body may be ascribed to the presence of water in the etching liquid, in particular when the content of hydrofluoric acid calculated on the quantity of water in the etching liquid is low, and is based on the idea of inactivating at least partially the water present in the etching liquid as far as the abovementioned side effect on the etching treatment is concerned.

According to the invention there is provided a method of treating a body of semiconductive material in which the body is chemically etched with an acid etching liquid which contains hydrofluoric acid, an oxidizing agent and a water-bonding agent.

The presence of the water-bonding agent counteracts the occurrence of etching pits and the roughening of the surface. The water-bonding agent may be sulphonic acid which may be added, for example, in the form of concentrated sulphuric acid to a desired percentage. Sulphuric acid provides sulphate ions to which water molecules are bonded by hydrogen bonds. The etching liquid may contain at least 30% by weight of sulphuric acid and in practice may con-

[*Price* 4*s.* 6*d.*]

Price 75p

tain at least 50% and in general not more than 85% will be used.

As with the known etching liquids it holds that the rate at which the liquid etches, is also dependent on the ratio between the quantities of the oxidizing agent and of the hydrofluoric acid in the liquid. If the etching liquid consists of hydrogen peroxide, hydrofluoric acid, sulphuric acid and water, the content of hydrogen peroxide may be at least 50% by weight and at most 150% by weight calculated on the quantity by weight of hydrofluoric acid present in the etching liquid. The content of hydrofluoric acid calculated on the quantity of water used in the etching liquid may be at least 10% by weight.

In order that the invention may readily be carried into effect it will now be described more fully, by way of example, with reference to the table below, giving examples of etching liquids and their action upon plate-shaped germanium bodies at a temperature of 25°C. The germanium bodies were obtained by sawing from a mono-crystalline germanium rod in directions at right angles to a <111> -axis followed by mechanical grinding to a thickness of 250 μ, in which a somewhat rough surface was formed. All the etching liquids were obtained by mixing a 48% aqueous solution of hydrofluoric acid, a 30% aqueous solution of hydrogen peroxide and concentrated sulphuric acid (96%). The decrease in thickness per minute stated in the table relates to a decrease in thickness by the action of the etching liquid on oppositely located surfaces of germanium bodies.

TABLE

Etching liquid	parts by vol. of HF-solution	parts by vol. of H_2O_2-solution	parts by vol. of concentrated H_2SO_4	% by weight of H_2O	% by weight of HF	% by weight of H_2O_2	% by weight of H_2SO_4	Decrease in thickness in μ/min.
A	1	2	1	42.7	10.6	12.7	34.0	43
B	1	2	2	32.7	7.8	9.3	50.2	32
C	1	2	4	22.7	5.1	6.2	66.0	10
D	1	2	6	17.9	3.8	4.6	73.7	6
E	1	2	8	15.1	3.0	3.6	78.3	5
F	1	2	10	13.2	2.5	3.0	81.3	3
G	1	1	4	17.3	5.7	3.4	73.6	8

It is noted that the decrease in thickness per minute as stated in the table is not dependent on the conductivity type and the specific conductivity of the body. The decrease in thickness per minute is larger at higher temperatures, namely increases approximately by 6% per °C.

Smooth surfaces were obtained using the freshly prepared etching liquids stated in the above table. The comparatively rapid etching liquids A and B give a noticeable rounding of the sharp edges of the bodies. The etching liquids C to G give more reproducible results and no rounding of sharp edges.

In the above table the etching liquids contain hydrogen peroxide as the oxidizing agent, while the etching effect is demonstrated with germanium bodies. However, the invention is not restricted to the use of hydrogen peroxide or to the etching of germanium bodies, for example, for silicon bodies according to the invention etching may be used with liquids which contain one or more oxidizing agents, hydrofluoric acid and a water-bonding agent.

WHAT WE CLAIM IS:—

1. A method of treating a body of semiconductor material in which the body is chemically etched with an acid etching liquid which contains hydrofluoric acid, an oxidizing agent and a water-bonding agent.

2. A method as claimed in Claim 1, in which the water-bonding agent is sulphuric acid.

3. A method as claimed in Claim 2, in which the etching liquid contains at least 30% by weight of sulphuric acid.

4. A method as claimed in Claim 2 or Claim 3, in which the etching liquid contains at least 50% by weight of sulphuric acid.

5. A method as claimed in any of Claims 2 to 4, in which the etching liquid contains at most 85% by weight of sulphuric acid.

6. A method as claimed in any of Claims 1 to 5 in which the oxidizing agent is hydrogen peroxide present in an amount of at least 50% by weight calculated on the quantity of hydrofluoric acid present in the etching liquid.

7. A method as claimed in Claim 6, in

which the content of hydrogen peroxide is at most 150% by weight calculated on the quantity of hydrofluoric acid present in the etching liquid.

8. A method as claimed in any of Claims 1 to 7 in which the content of hydrofluoric acid calculated on the quantity of water present in the etching liquid is at least 10% by weight.

9. A method of treating a body of semiconductor material according to Claim 1 substantially as herein described with reference to the specific examples.

10. A body of semiconductor material when treated by the method as claimed in any of the preceding claims.

T. D. THREADGOLD,
Chartered Patent Agent,
Century House,
Shaftesbury Avenue, London, W.C.2,
Agent for the Applicants.

Abingdon: Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1965.
Published at The Patent Office, 25 Southampton Buildings, London, W.C.2,
from which copies may be obtained.